Effect of Transmission Electron Microscopy Sample Preparation Methods on the Nanoscale Structure and Properties of Metallic Glasses

Gyuchul Park

Advised by Professor Jinwoo Hwang

Department of Materials Science and Engineering

The Ohio State University

Abstract

Metallic glasses (MGs) are new metallic alloys with excellent mechanical properties. However, practical applications of MGs are still limited due to the lack of understanding on their atomic structure. Since MGs have disordered atomic structure, it is difficult to obtain the structural information that directly connects to their important properties. Recently developed transmission electron microscopy (TEM) techniques, such as fluctuation microscopy, opened new possibility in understanding the structure-property relationships in disordered materials. However, it is important to understand the effect of the TEM sample preparation methods to the structure and the quality of the samples. In the present work, we demonstrate that the structure of the MG TEM samples can change depending on the sample preparation methods. We showed that the samples prepared using mechanical polishing changed its structure, while the samples prepared using focused ion beam (FIB) showed no apparent structural change. FIB method also had other benefits, including faster preparation time and high success ratio. However, concerns still remain because FIB is known for damaging the surface of the samples, and the extent of the surface damage is difficult to quantify in disordered materials, such as MGs. Regardless, we conclude that FIB is the most efficient and reliable technique for MG TEM sample preparation. On the other hand, since mechanical polishing makes the material plastically deformed, it may be useful for studying the nanoscale deformation behavior of MGs.

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Introduction

The purposes of the research were to prepare a high quality of metallic glass (MG) sample and to find the best method for measuring the structure of MGs. MGs were discovered by Pol Duvez at Caltech. First MGs were produced by liquid quenching. A molten metallic alloy was rapidly cooled down so that the atoms don't have time to be crystallized. [1] MGs are attractive materials because unlike to other metallic materials, they have disordered atomic structure. Since metallic glasses don't have crystalline phase, they don't have dislocations, which decrease theoretical yield strength of materials. Therefore, metallic glasses have higher strength than their counterparts. Additionally, MGs have very low viscosity in the supercooled liquid region above the glass transition temperature at high temperatures, which enables an exceptional casting ability. These excellent properties of MGs have made them a promising candidate material that can partially replace conventional alloys for structural applications. $Ti_{48}Zr_{20}Be_{15}V_{12}Cu_5$ was used as a metallic glass composite in the research.

In order to understand the properties of MGs, their structure-property relationship should be established by measuring the structure of MGs. However, it is difficult to determine the structure-property relationships of MGs due to their disordered structure. Recently, Prof. Hwang has overcome this problem and characterized the nanoscale structure of MGs using new TEM techniques, such as fluctuation electron microscopy (FEM) and electron diffraction. [4] The techniques require many electron diffraction patterns in order to extract reliable structural information from the disordered structure. They also critically depend on the quality of the TEM samples. It is therefore important to prepare TEM samples that have large thin areas without any structural damage caused by the sample preparation procedure itself.

Methodology

Mechanical polishing, electropolishing, and Focused Ion Beam were utilized in the research. Figure 1 represents the equipment used for the sample preparation methods.

Figure 1: Equipment used in the polishing process. (a) Allied High Tech mechanical polisher (b) Tenupol-5 Electropolisher (c) FEI Helios FIB

Focused Ion Beam

FIB uses a Ga ion beam, which can be focused on a nanoscale area, and therefore any nanoscale region of the material can be selected and prepared for TEM observation. The MG sample was mechanically polished until the thickness become 100 um. A layer of platinum was deposited on the area where we are interested in. Both sides of the region where we are interested in are removed with a Ga ion beam. Then the sample was tilted with respect to a Ga ion beam and almost cut. Once an omniprobe needle is welded to the sample, the sample is completely cut and lifted out for TEM observation. A few recent works have already implemented this method as an alternative to electropolishing for MGs.[4] The disadvantage of FIB is the structural damage on the surface of the sample. The ion milling can damage the sample surface or even alter the structure. In the case of crystalline materials, we can at least estimate the extent of the surface damage by directly observing the damaged layer in TEM. The estimation is, however, difficult

for MGs, because it is challenging to see the difference between the bulk MG and the damaged layer using simple TEM imaging.

Mechanical polishing

Mechanical polishing is based on surface polishing of materials using diamond embedded lapping films in a disk polishing machine.[2] The diamond embedded lapping films were used for grinding and polishing. The diamond embedded lapping films were placed on a spinning wheel of the mechanical polisher. The size of particle used as lapping films got finer from 30 um to 3 um with a lubricant of flowing water. There is an empirical rule, called "Rule of Three". Assumption is that a surface damage layer is three times thicker than the particle size in the lapping film. Mechanical polishing was performed based on the assumption in order to minimize the surface damage layer. Once the thickness of the sample became approximately 20 um, wedge polishing was performed (between 2° and 4°) with 1 um and 0.1 um of lapping films so that the tip of the sample becomes 10 um in thickness. For the final step, a polishing cloth is used with a lubricant of 0.05 um and 0.02 um of colloidal silica in order to improve the quality of the surface. There are a couple of advantages of this method. First, the surface can be relatively damage free, and second, a very large thin area can be achieved. There are, however, some disadvantages as well. Since this method relies on mechanical contact between the lapping film and the sample, it may induce plastic deformation of the sample, especially when the material is ductile, such as in metals. MGs are relatively brittle as compared to many pure metals, but they may still plastically deform when mechanically polished.

Electropolishing

Electropolishing is based on acid etching of the sample in an electrically biased environment. The MG sample was mechanically polished and thinned into 100 um in thickness before electropolishing is performed. The principle of the electropolishing is that a specimen is made the anode in an electrolytic cell. [3] A MG sample was punched with 3 mm diameter and placed in a sample holder. When a current was applied, a MG sample started to be etched. The sample got thinner and a hole was formed in the center of the surface. Once a hole was formed, electropolshing was stopped and the neighboring regions were used for TEM observation. 900 ml of methanol and 150 ml of Nitric Acid were used as electrolyte. The temperature of electrolyte was - 40 ℃ and applied voltage was 42 V. The low temperature kept by pouring liquid nitrogen into the electrolyte. Electropolishing has been known to produce damage free samples, and the procedure can be very fast. However, it is very difficult to get the right polishing conditions, and the success ratio of the procedure is relatively low. Also, it does not provide any control over the selection of the location of the thin areas.

Results

Figure 2 shows the structural data from the MG sample prepared by Focused Ion Beam. The STEM images show no damage on the surface of the FIB MG sample. There are two distinctive regions with clear contrasts: the brighter regions and the darker regions. Based on the nano diffraction pattern, the brighter regions are amorphous phase and the darker regions are crystalline phase. The amorphous phase looks very homogeneous as indicated by the nano diffraction pattern in (b) which shows no apparent azimuthal variation in intensity.

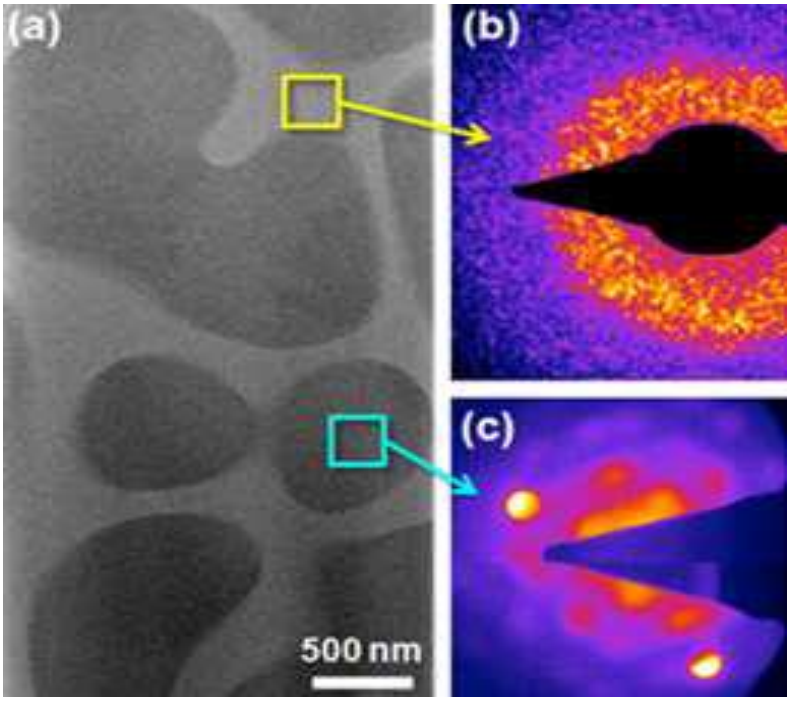

Figure 2: STEM image (left) and nano diffraction patterns (right) of the MG sample prepared by FIB

Figure 3 shows the structural data from the MG sample prepared by mechanical polishing. As shown in STEM image, the surface looks very different from the surface of the MG sample prepared by FIB. The MG sample is plastically deformed and sheared. According to the nano diffraction, the regions without any contrast, the area inside the yellow box, are amorphous phase and the regions with bright strips are crystalline phases. The amorphous phase looks inhomogeneous according to relatively large spots as represented in nano diffraction pattern. Also, the regions with bright strips, indicated as red arrow, were found, which were not present in the MG sample prepared by FIB. Circular features with ~50nm diameter are residual colloidal silica particles from the final mechanical polishing step.

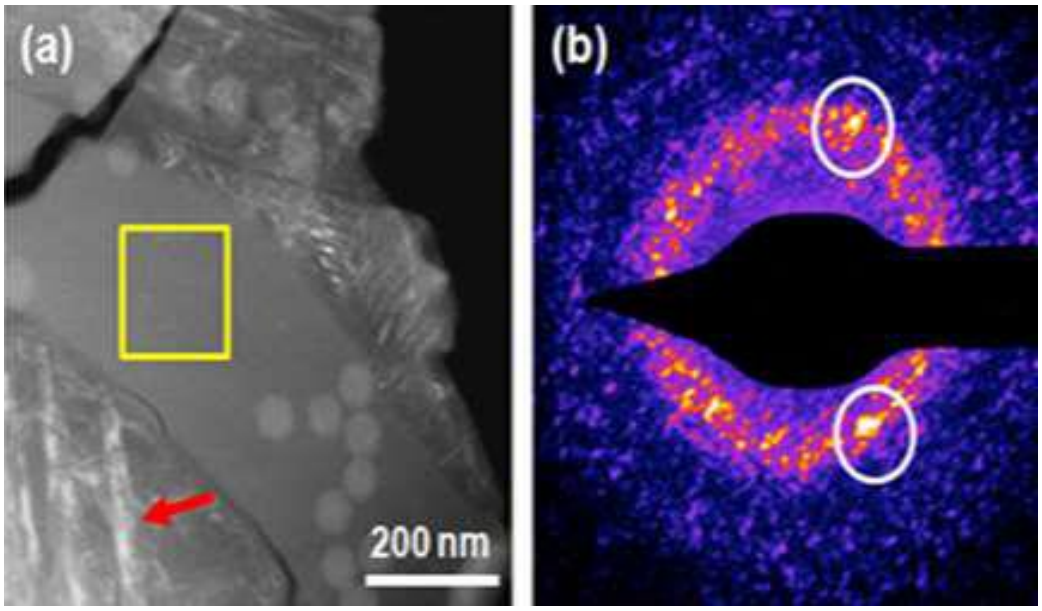

Figure 3: STEM image (left) and nano diffraction patterns (right) of the MG sample prepared by mechanically polished sample.

Figure 4 represents the MG sample prepared by electropolishing. A hole was successfully formed in the middle of the MG sample. However, the MG sample prepared by electropolishing did not yield any electron transmittance because the MG sample was too thick. Therefore, any structural data was not produced from the electropolished sample.

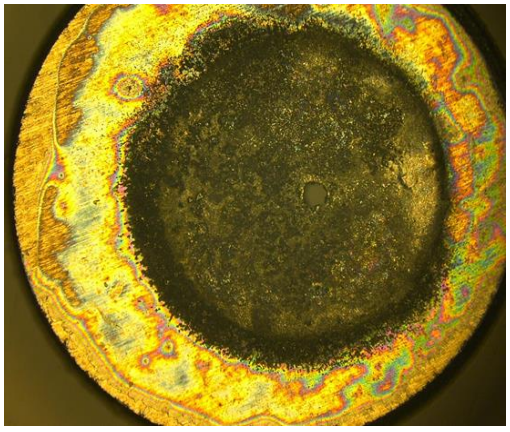

Figure 4: the MG sample prepared by electropolishing

Conclusions

A quality of the surface of the MG sample depended on the sample preparation methods. For Focused Ion Beam, there was no any structural damage on the surface of the MG sample. Also, the amorphous phase looked quite homogeneous. For mechanical polishing, compared to the MG sample prepared by FIB, not only were plastic deformation and shearing found on the surface of the MG sample, but also the amorphous phase looked inhomogeneous. Also, the bright stripe regions were seen that were not present in FIB sample. The plastic deformation caused during the mechanical polishing process might change the structure of metallic glasses. For electropolishing, the polished sample was too thick to have diffraction pattern. It was much more difficult to control the electropolishing condition than other methods. In conclusion, FIB is the best method for studying the structure of metallic glasses. FIB ensures fast and reliable sample preparation process, and yields fairly good quality samples. Even though mechanical polishing is not appropriate for studying structure of metallic glasses, it might be useful to study plastic deformation behavior of metallic glasses and metallic glasses composites.

Future Works

While the mechanically polished sample showed about 20% electron transmittance, the FIB sample showed about 5% electron transmittance. That means thickness of the FIB sample was thicker than the thickness of the mechanically polished sample because electron transmittance is inversely proportional to the thickness of the sample. The thick thickness might change the diffraction pattern because multiple scattering can happen in thick samples and make diffraction speckles smaller. Therefore, a thinner MG sample needs to be prepared by FIB next time. In

addition, FIB may induce small surface damage that was not detected in STEM image. We will use Fluctuation Electon Microscopy to check if there is any measurable change in the structure due to FIB damage. The structure at the interface between the glass and the crystal particles will be examined as well. This will provide useful insights on the superb mechanical properties of metallic glass composites. Lastly, since we failed to acquire the structural data from the electropolished sample, we will try electropolishing again in order to see if the MG sample prepared by electropolishing has the highest quality or not.

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